

# PROCESS FOR PREPARING CERAMICS COMPOSITE SINTERED BODIES

## BACKGROUND OF THE INVENTION

### (1) Field of the Invention

The invention relates to a process for preparing glass or glass-ceramic composite sintered bodies excellent biocompatibility, particularly such sintered bodies useful as artificial bones or tooth roots. The invention also relates to novel ceramics composite sintered bodies excellent in biocompatibility.

### (2) Prior Art

Various ceramics materials have been proposed together with apatites as materials for hard tissues of living bodies such as artificial bones or artificial tooth roots. Among them, calcium phosphate glasses or glass-ceramics have drawn particularly attention as materials directly binding to bones, and have been prepared according to the melting method, the sol-gel method and other such methods.

On the other hand, ceramics materials which have hitherto been proposed as materials directly binding to bones are generally inadequate in strength. As a result, members consisting of ordinary ceramic materials have to be made thick at the part in living bodies where the load is high, and the range of applicability thereof have been limited.

Under the circumstances, for solution of such problems it has been proposed to incorporate various ceramics fine particles, short fibers, whiskers, etc. in the ceramics matrices of the aforesaid ceramics members as reinforcing materials. For example, use of fibers or whiskers of metals, ceramics or glass as a core material (Japanese Patent Publication for Opposition Purpose (hereinafter referred to as "J.P. KOKOKU") No. 59-219), use of carbon fibers and mineral fibers (in Japanese Patent Unexamined Published Application (hereinafter referred to as "J.P. KOKAI") Nos. 59-57970 and 59-57971), and use of ceramics short fibers or whiskers (J.P. KOKAI No. 61-234867) have been proposed. However, all of the ceramics disclosed in the above publications are prepared by mixing a matrix component with a reinforcing material in a dry or wet state and sintering the mixture, and a process for preparation of ceramics by the sol-gel method is not disclosed therein.

On the other hand, glass has hitherto been prepared according to a melting method or VAD (Vapor-Phase Axial Deposition method), and glass-ceramics have been obtained by subjecting glass to a crystallizing treatment. However, sol-gel methods have the advantages that glass-ceramics can be synthesized at a low temperature, glass-ceramics having high purity can be obtained, and no limitation due to range of vitrification arises, which is different from the case in a melting method, and thus sol-gel methods have attracted attention. As for sol-gel method, J.P. 60-246254 discloses a process by a sol-gel method of preparing ceramics wherein whiskers etc. are dispersed in the ceramics matrix, by mixing a dispersion of ceramic particles and/or whiskers in water with a metal alkoxide. However, the metal alkoxides used therein are those for machinery members such as aluminum alkoxides, and there is no disclosure therein about preparation of calcium phosphate ceramics useful for living body materials.

Thus, there has been desired a process for effectively preparing reinforced calcium phosphate ceramics,

which have recently drawn particular attention, by a sol-gel method.

## SUMMARY OF THE INVENTION

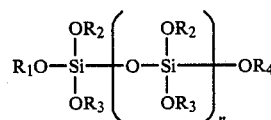
The primary object of the invention is to provide an excellent process for preparing composite sintered bodies wherein calcium phosphate glasses or glass-ceramics, as a matrix having high biocompatibility, is reinforced with (D-1) ceramics fine particles and/or (D-2) ceramic short fibers and/or whiskers.

Another object of the invention is to provide novel ceramic composite sintered bodies containing ceramic fine particles, ceramics short fibers and/or whiskers as reinforcing materials.

The invention has been accomplished based on the finding that when gel is formed by reacting a certain silicic acid ester, a certain phosphorus compound and a certain calcium compound with water, the above object can effectively be attained by carrying out the gelation reaction in the presence of ceramics fine particles, ceramic short fibers or whiskers.

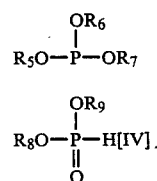
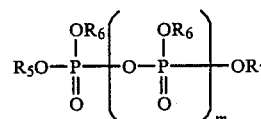
More specifically, the invention provides a process for preparing a glass or glass-ceramic composite sintered body which comprises reacting

(A) at least one silicic acid ester represented by the general formula (I):



wherein  $\text{R}^1$  to  $\text{R}_4$  are each hydrogen or a group represented by  $\text{C}_x\text{H}_{2x+1}(\text{OC}_2\text{H}_4)_y$  wherein  $x$  is 1 to 5, and  $y$  is 0 to 10, provided that  $\text{R}^1$  to  $\text{R}_4$  are not all hydrogen at the same time, and  $n$  is 0 to 20;

(B) at least one phosphorus compound represented by the general formula (II), (III) or (IV):



wherein  $\text{R}_5$  to  $\text{R}_9$  are each hydrogen, an alkyl group having 1 to 5 carbon atoms, a phenyl group or an aralkyl group having 7 to 10 carbon atoms, and  $m$  is 0 to 10;

(C) at least one compound selected from the group consisting of calcium salts and calcium compounds represented by the general formula (V)



wherein  $\text{R}_{10}$  represents an alkyl group having 1 to 5 carbon atoms; with water in the presence of the following component (D-1) and/or the following component